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A POSSIBLE DOMESTIC SOURCE OF VEGETABLE TANNIN

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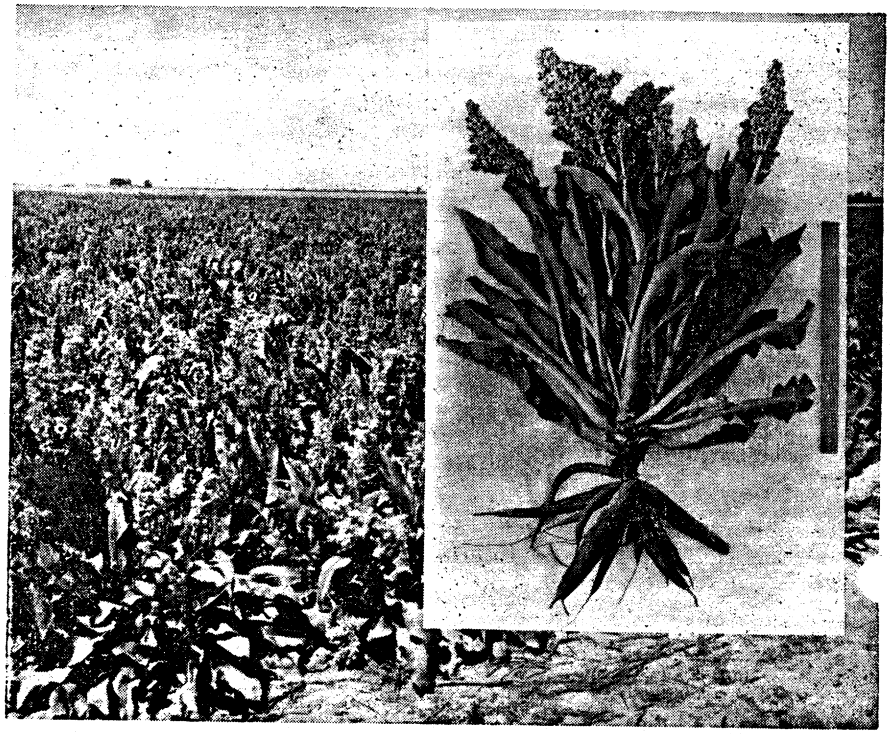
Introduction

It is quite generally known that there is a definite shortage in the readily available supplies of domestic vegetable tannins. It may not be fully realized, however, how serious a situation might develop nationally in the tanning industry if the supplies of imported vegetable tannins were completely cut off or heavily curtailed as a result of a war emergency.

In this connection it is of interest to note that the domestic production of vegetable tannins has been decreasing over a period of years. In 1950 it reached a new low of about 15% of our consumption of approximately 112,000 short tons of 100% tannin.[1] To provide security for its tanning industry this country must have a more adequate supply of tannins which can be increased or lowered as required to meet tanning needs. This country should not be dependent upon imports for 85% of the vegetable tannins that it uses. The question naturally arises: how can domestic tannin production be increased? The answer, which is quite self-evident, is by development of new tannin supplies. This might be accomplished by development of suitable synthetic tannins or by producing on a large scale vegetable tannins from entirely new sources or from unused but available supplies.

During the past several years there have been developed a number of synthetic tannins which have shown quite promising results when used alone for retanning, or for blending with other tannins for the production of certain types of leather. In general, the synthetic tannins have found most promising application in the tanning of lightweight leathers. An examination of manufacturers' recommended uses of these materials has revealed that only two of these synthetic tannins are apparently suitable for heavy leather tanning.[2] These, although they could be used as the only tanning agent, are not recommended for such use because of their much higher tan unit costs as compared with those of the vegetable tannins normally used. Consideration, with regard to increased use of synthetic tannins in times of emergency, must be given to the fact that some of these require for their production chemicals such as aldehydes and phenols, which are considered as highly critical and strategic materials.



FIELD of maturing Canaigre, second season of growth. Inset shows detail of plant, and gives an idea of approximate size (that's an 18-inch rule at right).

With this article, prepared especially for the **Shoe and Leather Reporter,** we present the first really comprehensive report on this country's experiments aimed at developing a new and practical source of tannin from Canaigre crops. These experiments appear to be the most promising of their kind to date. The authors explain the nature of the Canaigre plant, methods of cultivation, methods and processes involved in developing a workable tannin from the plants. Dr. Rogers is of the Staff of the Eastern Regional Research Laboratory, Philadelphia, one of the Agriculture Department's key research laboratories; and Dr. Pultz is a member of the Bureau of Plant Industry, Soils, and Agricultural Engineering, Beltsville, Md. The project is carried on under the aegis of the U. S. Department of Agriculture.

The domestically produced tannins now in use are those obtained from wood from blight-killed chestnut trees, oak bark, hemlock bark, sumac leaves, and pecan shells. Of these, chestnut wood has recently furnished more than 85%. When the chestnut tannin supply is exhausted we will be almost entirel, dependent upon imported tannins unless new domestic supplies a·

developed. Such new supplies can be obtained by salvage and utilization of available barks[1] and by the development and production of tannin from plants that can be grown as farm crops. This paper deals with research on the development of canaigre, a potential source of tannin, that can be produced as a tannin crop.

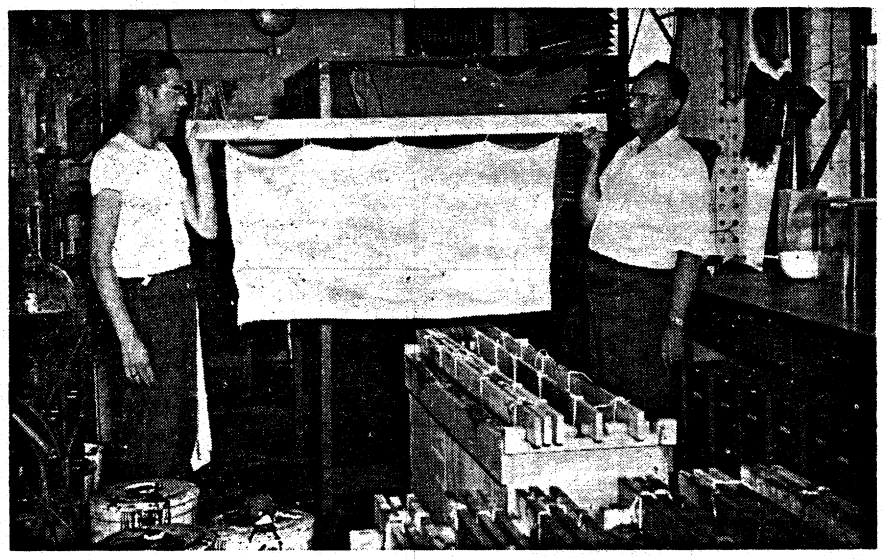
History

The Indians and Mexicans have used canaigre for tanning for more than a century. The first botanical specimens were probably those collected near El Paso, Texas, by Thurber and sent to Torrey,[3] who described the plant in 1859 and gave it the name *Rumex hymenosepalus*. The first published analysis of canaigre roots, given by Voelcker in 1876, showed a tannin content of 23.16%.[4] In 1878 the Commissioner of Agriculture published the analyses of two samples of roots collected in Texas. These showed tannin contents of 26.2 and 26.6%.[5]

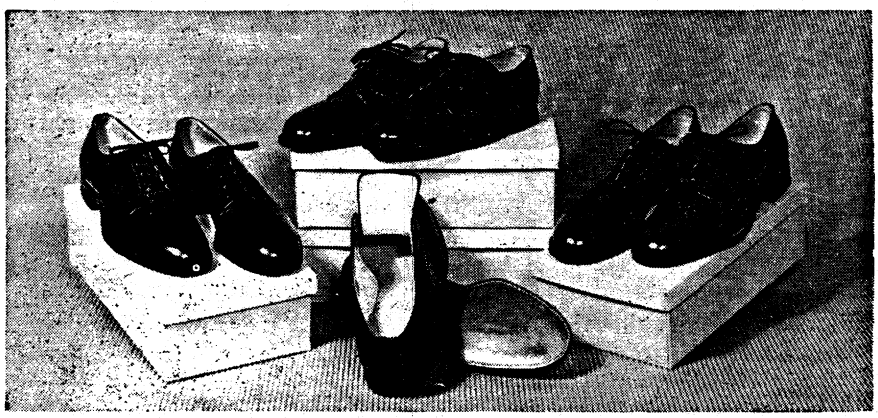
Between 1880 and 1910 more than 50 publications dealing with canaigre were issued. These reported studies of canaigre conducted by workers in the State Experiment Stations of Arizona, New Mexico, Texas and California,[6, 7, 8, 9, 10, 11, 12, 13] and by independent workers. They reported tannin contents and the results of studies on cultivation harvesting and extract preparation.

Trimble[14] reported that canaigre roots were exhibited at the New Orleans exposition in 1885 as a new tanning material. Gulley[15] stated that in 1887 the first carload shipments of canaigre roots were made from Tucson, Arizona, to Glasgow. From 1890 to 1892 several thousand tons of sliced, dried roots were shipped to Great Britain and Germany. A factory for making extract was established at Deming New Mexico, in 1892. An attempt to cultivate canaigre and produce roots without irrigation was unsuccessful. In 1893 the Arizona Agricultural Experiment Station exhibited canaigre extract containing 60% tannin at the World's Fair.

Although tests had shown canaigre to be a good tanning material,[16] it did not become established as a regular source of tannin. This was possibly due to difficulties encountered in growing it as a crop, lack of facilities for collecting and transporting wild roots and to difficulties in the economic production of a good quality extract. There was little further work done on its development until active research on canaigre was undertaken in the U. S. Department of Agriculture.[17, 18]



C. W. Beebe and W. S. Kip Preparing to Immerse Trimmed White Hide Bend into Tanning Liquor Containing Canaigre Blend.



Test Shoes — The Pair in the Center Foreground has Canaigre-Tanned Left Sole and Commercially-Tanned Right Sole.

The Canaigre Plant

The canaigre plant, botanically known as *Rumex hymenosepalus Torr,* is sometimes called tanner's dock. It is native to southwestern United States and northern Mexico. It grows from 1 to 3 feet high and the spread of its rather large leaves is sometimes as much as 18 inches. The tuberous roots of canaigre are somewhat like those of the sweet potato or dahlia in appearance. When moisture-free, they contain tannin of the "condensed" type in amounts ranging usually between 25 and 35%. The roots also contain starch and sugars ranging, respectively, from 20 to 40% and from 8 to 20%. Examination has disclosed that roots which have pink or red interiors have more tannin and less undesirable nontannins than those which have distinctly yellow interiors.

Development Program

In 1937 the Department of Agriculture added to its program on the development of domestic tannin supplies the research on canaigre.[17] In the beginning the work was conducted on a relatively small scale and progress was slow.[18] More recently, aided by appropriations furnished by the Research and Marketing Act for agricultural

and industrial research for the production of Critical and Strategic Materials, the canaigre investigations have been largely expanded.

This research, from its beginning, has been conducted on a cooperative basis. The Bureau of Plant Industry, Soils, and Agricultural Engineering conducts all phases of the work relating to the establishment of canaigre as a crop. Improved strains are being selected and increased, and effective methods are being determined for propagating, cultivating, harvesting, and storing the crop, and for controlling plant diseases and insect pests. The Bureau of Agricultural and Industrial Chemistry, through its Eastern Regional Research Laboratory, conducts all laboratory work, evaluates roots for tannin content, studies the effect on tannin content of various field treatments, makes all processing and extraction studies, prepares tanning extracts, conducts experimental tanning and appraises the leather-making qualities of canaigre tannin.

Agronomic Studies

Canaigre grows naturally in the semi-arid sections of southwestern United States where the climate is characterized by warm winters and hot summers. Wild plants make their growth during the months from September to May, growing slowly during the winter months and making rapid growth during spring.

To determine locations with climate and soils adapted to the growing of canaigre, test plantings using wild roots collected near Las Cruces, New Mexico, were made near Las Cruces and at ten locations in Texas. Later, additional test plantings were made in Arizona, Florida, Georgia, South Carolina, Alabama, Louisiana, Mississippi, and California. In these plantings best results were obtained in Arizona, Texas, New Mexico, and California where canaigre can be grown as a winter crop under irrigation. The agronomic studies have since been centered in this area, principally in Arizona.

Wild plants collected from different localities furnished roots that were used as planting stock in the early field experiments and were found to be extremely variable in habits of growth and in shape, color, and tannin content of the roots. To obtain the best strains for use as a cultivated crop, samples of wild roots were collected from more than 100 locations in seven southwestern States. The strains highest in tannin content were obtained from Arizona, Nevada, California, and Utah, and ranged from 31.3 per cent to 36.1 per cent (moisture-free basis). Progress is being made with a breeding program to develop high-yielding strains with high tannin contents and other desirable agronomic and chemical characteristics.

Experimental plantings in Arizona, New Mexico, and Texas have demonstrated that canaigre can be propagated successfully by planting whole roots, root crowns, or seed. Plants grown from seed require two winter growing seasons to produce a harvestable crop, the plants being dormant during the hot summer period. Root crowns used as planting stock produce a crop in one growing season at a somewhat higher cost per ton of roots than is the case with seed. Both methods of propagation appear to have possibilities in the commercial culture of canaigre.

Many of the cultural methods and machinery used in producing sugar beets and potatoes can be used for canaigre. Present experimental plantings are grown on raised vegetable beds with either one or two rows of plants on each bed. This arrangement allows the crop to be furrow-irrigated and facilitates the harvest of the roots with a modified potato harvester. Seed can be planted with regular vegetable seeders and standard potato planters can be used to plant root crowns.

Variation in spacing of plants in the rows and between the rows apparently does not materially affect the tannin content of the roots. Studies are in progress to determine the effect of various plant spacings on the yield of roots. At the present time seed plants are spaced 3 to 6 inches apart in the row, and root crowns 12 to 18 inches apart.

Canaigre can be grown in soils having a wide variety of textures, but like other root and tuber crops it grows well in the lighter sandy loam soils. Several tests have shown that root yields of canaigre can be increased by applications of fertilizers containing nitrogen and phosphorous. The tannin content of the roots apparently is not materially affected by fertilizer applications even when the root yields are increased. In the areas where canaigre is now being grown, rainfall during the growing season is normally very low. A limited amount of irrigation is required to produce a good crop. Results of experiments in southern Arizona indicate that 1.5 acre feet of irrigation water are sufficient to produce a good crop, most of it being applied during the periods of rapid growth in fall and spring.

Studies of the changes in the composition of canaigre roots have shown that roots grow most rapidly during the months of April and May. During that same period there is also the most rapid increase in tannin. During February, March, and April the total sugar content decreases quite rapidly, and the starch content increases very rapidly during the months of March and April. The results of these studies indicate clearly that the optimum time to harvest canaigre roots as regards tannin content, purity, and leachability, is during the months of July and August.

Yields of roots obtained from experimental plantings have varied considerably. In some plot tests yields of more than 10 tons per acre per year were produced, but in field tests when several acres were planted, yields were lower. On a basis of results obtained to date, it is anticipated that an average yield of at least 10 tons per acre per year can be produced.

The roots when first dug usually contain between 65 and 75 per cent moisture, most of which should be removed before shipment in order to lower transportation costs. Drying of whole roots has not been successful, but shredded roots can be dried in mechanical driers or by open air field drying. In southern Arizona thinly shredded roots spread at the rate of 1 to 1.25 pounds per square foot on a hard surface such as cement have been successfully dried in 4 to 8 hours on clear days at temperatures of 100° F. or above. On cloudy, humid days longer drying periods would be required. Too deep spreadi

or cloudy, humid weather during the drying period has resulted in fermentation, mold growth, and material losses in tannin and sugar.[19] Since both mechanical and field drying operations represent items of considerable expense, methods for safe storage of freshly dug roots are under study. Such storage would make it possible to hold the harvested crop for several months and thus furnish raw material to the extraction plant as needed to give nearly continuous operation. The storage procedures now under study include storage in pits and in piles, both covered with soil, and open air storage under sheds.

From beginnings with small experimental plots the plantings have been increased and now occupy from one to twenty acres located in various areas, but principally in Arizona. Nineteen acres were harvested in 1951, and 18 acres in 1952. It is expected that there will be about 35 acres ready for harvest in 1953. The production of canaigre roots in these larger quantities has made it possible to furnish roots for the processing studies at the Eastern Regional Research Laboratory.

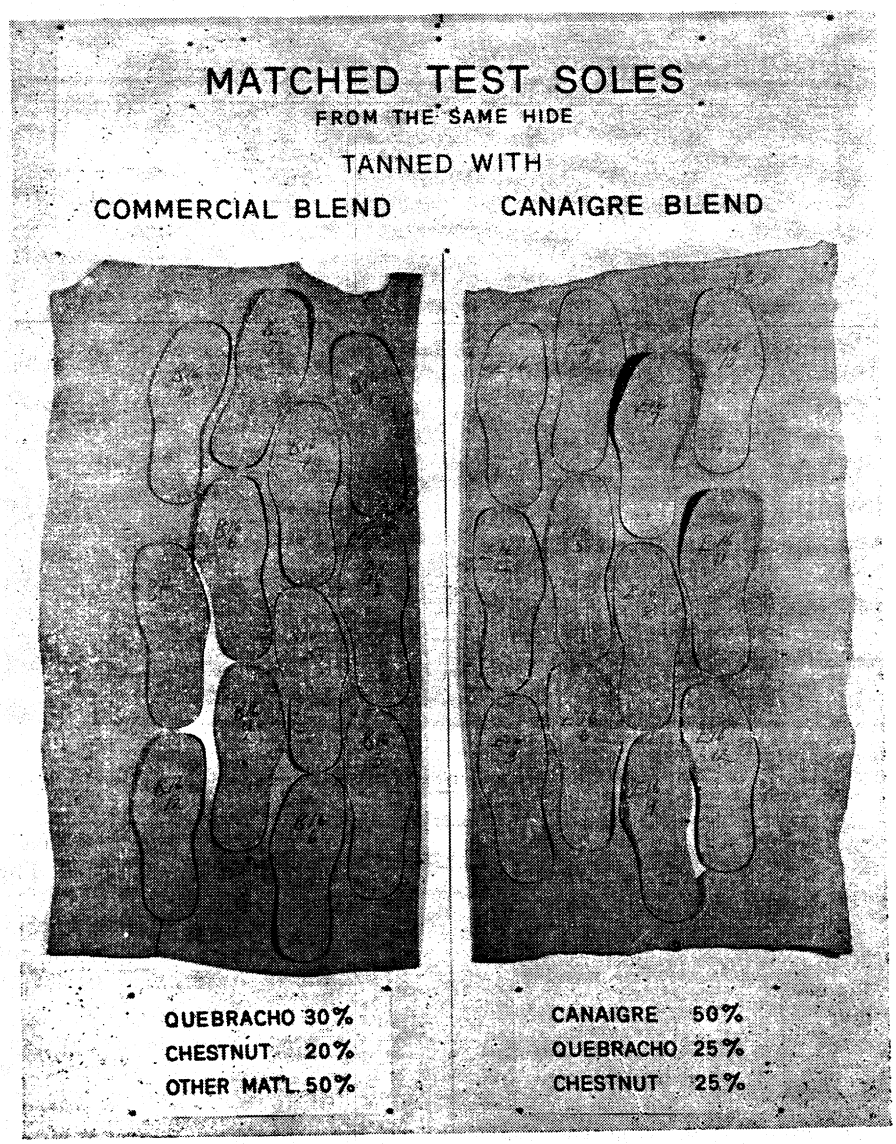
Processing Studies

There have been assembled and furnished to the Eastern Regional Research Laboratory about 34 tons of shredded dried canaigre roots and additional quantities will become available from the 1952 harvest.

The processing of canaigre roots into high quality tanning extract presents several major problems. These differ from problems normally encountered in making extract from barks or woods because canaigre roots contain starch and sugar. If hot water is used for extracting the tannin, the starch gelatinizes and prevents efficient extraction. Tannins that are difficultly soluble are less soluble in cold water than in hot water. The sugars present are easily soluble and thus come out with the tannin irrespective of how it is extracted. The presence of sugar raises the non-tannin content of the liquors and lowers the purity of the tanning extract. Other factors that require study are methods for the control of mold in canaigre liquors and the reduction of insolubles. Considerable progress is being made in meeting these problems.

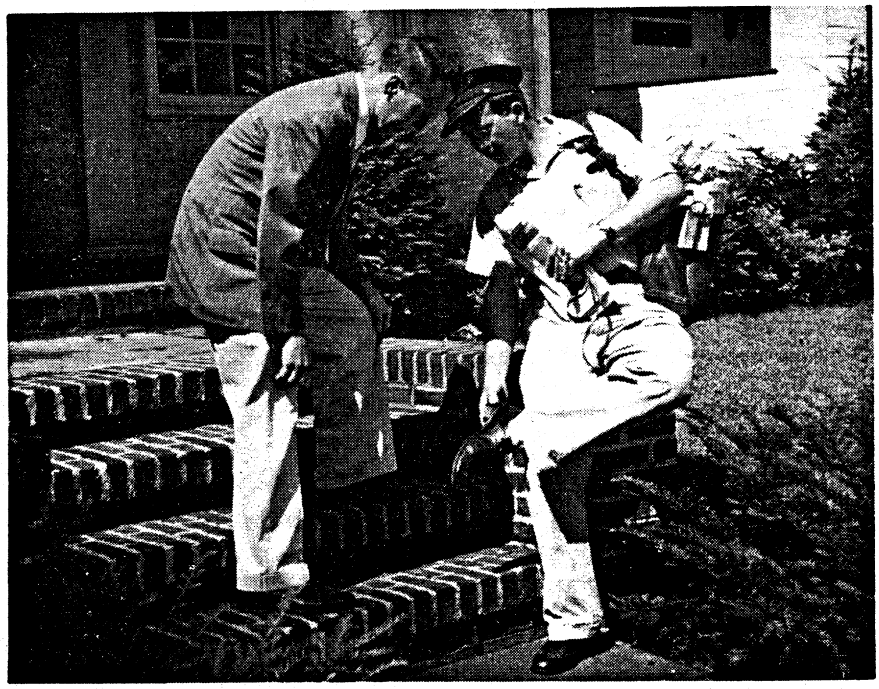
Various extraction procedures have been studied. These include: counter-current battery extractions of thin canaigre slices or shreds using water at 45° to 50° C., a temperature below gelatinization point of starch; counter-current extraction of finely comminuted roots with water at 40° to 45° C., requiring the separation of solids by filtration or centrifuging; [20, 21] and extraction by similar methods using a 50% acetone-water solution.[22, 23] Later results were obtained using 17% isopropyl alcohol in a Kennedy type extractor. By use of solvent-water extraction, tannin recoveries were increased about 10% above those obtained by water extraction. However, it appeared to be preferable to use a water extraction process because of the evident disadvantages in solvent-water extraction. These include solvent recovery and equipment costs, fire hazard and the fact that the extract made by solvent-water extraction showed higher insolubles when dissolved in water and when used in tanning.

By use of the countercurrent water extraction procedure, it was possible, on a laboratory-scale, to extract from 75 to 85% of the total tannin from high quality canaigre



Matched Test Soles Cut from Right and Left Bends of the Same Hide.

roots of the red type. With a Kennedy extractor, which operates countercurrently and is obtainable in commercial-scale capacities, the tannin recoveries were considerably lower than those obtained with small scale laboratory equipment. Use of the present process and the Kennedy equipment, however, will provide a good quality canaigre extract in quantity sufficient for use in semicommercial tanning tests. Further study will be devoted to improvement of the extraction efficiency. This may be accomplished by modification of the present process or the equipment.



Postmen Cooperate in Making a Service Test of Canaigre-Tanned Leather.

The problem of improving the purity of the liquors extracted from canaigre roots is one of removing or destroying the sugars. These are water soluble and are extracted with the tannins. Fermentation into alcohol would appear to be a simple solution, but the answer is not so easy. Canaigre roots contain some substance which inhibits the natural growth of the yeasts that change sugars into alcohol. This problem has been solved by studying the various types of bacteria that will grow in canaigre liquors and isolating and using a type that will destroy sugars but will not affect canaigre tannin.[24, 25] Bacteria belonging to the *Aerobacter aerogenes* group have been found which meet these conditions. They destroy a large part of the sugars and thus produce liquors yielding extracts of high purity (ratio of tannin to soluble solids). For example, purities have been raised from 53.0 to 68.4. This fermentation produces 2, 3 butylene glycol, acetoin and a relatively small amount of ethyl alcohol. The utilization of these materials as by-products does not appear promising inasmuch as their value is not high and their recovery from the fermented liquors is not easy.

The preparation of the liquors extracted from canaigre roots for concentration to tanning extracts includes the following steps: screening and filtering to remove coarse solids, fermenting to destroy sugars and centrifuging for further clarification. Liquors prepared in this manner are ready for vacuum evaporation to concentrate them to liquid extracts and subsequent spray or drum drying to yield spray-dried, powdered extracts.[26]

From canaigre liquors obtained by extracting roots in a small Kennedy extractor there have been prepared 700 lbs. of powdered canaigre extract which showed the following analysis:

No. 58077

Spray-dried Canaigre Extract

Total Solids	95.18%
Soluble Solids	92.05%
Insolubles	3.13%
Nontannins	31.64%
Tannin	60.41%
Purity—basis of Soluble Solids	65.63%

The quality of this extract as indicated by its analysis would place it in a class with some of the best commercial tanning extracts. This extract has not been bisulfited. It will respond, however, to bisulfiting, yielding an extract higher in tannin and lower in insolubles.

Canaigre Tanning

During the development studies of canaigre, several small-scale tanning tests have been made in the laboratory. In some of these tests powdered canaigre root has been used and in others tanning has been done in liquors prepared from canaigre extract.[27] Sheepskin leathers of the hatband type have been successfully tanned with powdered canaigre root used in the same manner that ground sumac leaf is used and also by canaigre extract. Goatskin leathers have been tanned with canaigre extract and retanned with aluminum salts to give leathers suitable for bookbindings. Calfskins have been tanned entirely with canaigre extract and have been retanned with canaigre following chrome tannage to give satisfactory leathers. Canaigre extract has been used successfully alone and in blends with other vegetable tanning materials to tan leathers of the sole leather type on a laboratory-scale. A cooperating laboratory has blended canaigre with Orotan on a 75 to 25% tannin basis to produce a satisfactory heavy leather tannage.[28]

In order to obtain definite information on the tanning properties of canaigre when used as the principal tanning agent in sole leather tanning, sole leather bends were tanned. The left bends were tanned with a blend in which 50% of the tannin was canaigre and 25% each of quebracho and chestnut. The right bends from th

same hides were tanned with a commercial blend of several vegetable tannins in which quebracho and chestnut tannin constituted 50% of the total tannin and in which there was no canaigre tannin. When the tannages were completed the leather in which the canaigre tannin was used compared very favorably with the commercial tannage in color, thickness, weight yield, and general appearance. The canaigre leather appeared to be equal in every respect to the commercially-tanned leathers.

Canaigre Leather Service Tests

To study the durability of the canaigre-tanned leather in actual service, the two leathers described above were used as soles in making 70 pairs of experimental shoes. In some pairs the canaigre leather was used on the right shoe and in others on the left shoe. In each case the mate shoe was soled with the commercially-tanned sole leather. The pairs of soles were selected so that they always came from corresponding locations on opposite sides of the same hide. This was done so that differences in durability of leather from different hide locations would be balanced. When the wear is completed on the first set of soles the shoes will be tapped, the canaigre leather being placed on the opposite shoe. This will balance differences in individual wear between right and left foot. The wearing test is made possible through the cooperation of 68 mail carriers from Post Offices located in the vicinity of the Eastern Regional Research Laboratory. (A report giving details of the tannage of the leathers and the results of the service tests will be prepared for publication at a later date in the *Journal of the American Leather Chemists Association.*)

Semiworks Extraction Plant

There is under construction at the Eastern Regional Research Laboratory a semiworks plant for the extraction of canaigre tannin and the preparation of canaigre extract. This plant provides for the countercurrent water extraction of dried, comminuted canaigre roots, the filtration, fermentation and centrifuging of liquors, and for vacuum concentration and spray drying to produce powdered canaigre extract. It is expected that this plant will produce canaigre extract of acceptable commercial quality and fully adequate in quantity for use in conducting semi-commercial tanning tests. From the data obtained it should be possible to make estimates of tan unit production costs.

Summary

Canaigre roots and seed to serve as planting stock have been collected from wild plants in seven states. Arizona, Texas, New Mexico, and California were found to have soil and climate adapted to the growing of canaigre.

Canaigre has been successfully propagated by means of seed, roots, and root crowns. Methods of cultivation have been investigated. Canaigre has been produced experimentally as a farm crop, using standard equipment for planting and cultivation, and has been harvested with machinery adapted from commercially available equipment.

Yields of canaigre roots approximating 10 tons per acre per year have been produced in experimental plantings.

Tonnage lots of canaigre roots have been shredded and air-dried and made available for extraction studies.

Processing studies have shown that tannin can be effectively extracted from canaigre roots even though they contain starch.

The purities of canaigre liquors have been improved by destruction of sugars, accomplished by fermentations with *Aerobacter aerogenes* without destruction of tannin.

High quality tanning extract has been made that compares favorably with commercial extracts in tannin content and tanning properties.

Canaigre extract has been successfully used in the experimental tanning of light and heavy leathers, in tanning alone and in blends, and for retanning.

Sole leather tanned with a blend containing 50% canaigre tannin has been made and compares favorably as regards thickness, weight yields and color, with leather made with a commercial tanning blend.

Shoes have been made in which canaigre-tanned soles are being compared in actual service tests with soles tanned with commercial tanning blends.

A semiworks extraction plant for the preparation of tonnage lots of canaigre extract for use in semi-commercial tanning tests is under construction.

REFERENCES

1. Rogers, Jerome S., Northeastern Wood Utilization Council, Bul. No. 39, "Tannin from Waste Bark," pp. 17-28, Sept. 1952.
2. Private Communications.
3. Torrey, John, Report of the United States and Mexican Boundary Survey, Vol. 2, p. 177 (1859).
4. Voelcker, Rudolph, F. G., American Jour. Pharm., 48, 49 (1876).
5. Report of United States Commissioner of Agriculture 1878, p. 119.
6. Collingwood, C. B., et al, Arizona Agricultural Experiment Station, Bul. No. 7 (1893).
7. Forbes, Robert H., Arizona Agricultural Experiment Station, Bul. No. 21 (1896).
8. Blount, A. E., New Mexico Agricultural Experiment Station, Bul No. 8, p. 35 (1892); No. 11 (1893); No. 14 (1894).
9. Hare, R. F., New Mexico Agricultural Experiment Station, Bul. No. 49 (1903).
10. Harrington, H. H. and Adriance, D., Texas Agricultural Experiment Station, Bul. No. 38 (1896).
11. Bonner, C. S., California Experiment Station Annual Report, p. 123 (1890).
12. Hilgard, E. W., California Experiment Station, Bul. No. 105 (1894); revised (1895), p. 186.
13. Colby, George E., California Experiment Station Report, p. 186 (1897).
14. Trimble, Henry, American Journal of Pharmacy, 61, 395 (1889).
15. Gulley, F. A., Agricultural Science, 8, 320 (1894).
16. Eitner, W., Der Gerber, May 1891; Der Gerber, 135, 149, 150 (1893); Der Gerber, 232 (1897).
17. Frey R. W. and Sievers, A. F., Jour. American Leather Chemists Assoc., 35, 647 (1940).
18. Rogers, J. S. and Russell, G. A., Jour. American Leather Chemists Assoc,, 39, 467 (1944).
19. Russell, G. A., et al., Jour. American Leather Chemists Assoc., 39, 479 (1944).
20. Beebe, C. W., et al., Jour. American Leather Chemists Assoc., 41, 161 (1946).
21. Cordon, T. C., et al., Jour. American Leather Chemists Assoc., 42, 118 (1947).
22. Luvisi, F. P. and Rogers, J. S., Jour. American Leather Chemists Assoc., 43, 166 (1948).
23. Luvisi, F. P., et al., Jour. American Leather Chemists Assoc., 44, 707 (1949).
24. Cordon, T. C., et al., Jour. American Leather Chemists Assoc., 42, 128 (1947).
25. Cordon, T. C., Jour. American Leather Chemists Assoc., 45, 485 (1950).
26. Rieder, Robert M., et al., Jour. American Leather Chemists Assoc., 46, 188 (1951).
27. Beebe, C. W., et al., Jour. American Leather Chemists Assoc., 46, 197 (1951).
28. Letter from H. G. Turley, Rohm & Haas Company.